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<b>(54) Title:</b> METHOD OF PRODUCING A THERMOPLASTIC POLYMER PREFORM AND AN ARTICLE PRODUCED THEREFROM		
<b>(57) Abstract</b>  A method of producing a thermoplastic polymer preform having at least a crystalline finish portion comprising: (i) providing a thermoplastic polymer composition comprising a thermoplastic polymer and at least one reheat rate increasing additive; (ii) forming a preform from the thermoplastic polymer composition, wherein the preform comprises a finish portion and a body portion; and (iii) exposing at least the finish portion of the preform to energy until crystallized.		

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## METHOD OF PRODUCING A THERMOPLASTIC POLYMER PREFORM AND AN ARTICLE PRODUCED THEREFROM

### Related Application

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This application claims priority to provisional patent application Serial No. 60/086,924, filed May 27, 1998, which is incorporated herein by reference in its entirety.

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### Background of the Invention

#### Field of the Invention

The present invention relates generally to the field of processing thermoplastic polymers and forming thermoplastic articles, and more particularly to a method of crystallizing a thermoplastic polymer by introducing a reheat rate-increasing additive into the thermoplastic polymer and processing same.

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#### Description of Related Art

##### *1. Reheat Rate-Increasing Additives in Blow Molding Applications*

The use of polymer compositions, particularly compositions comprising poly(ethylene terephthalate) or copolymers thereof (hereinafter collectively referred to as "PET"), for example in the form of films, bottles and other containers is well known. When bottles or other containers (hereinafter collectively referred to as "containers") are used for containing fluids, e.g., water, juices and carbonated drinks, container-forming compositions, in the form of polymer chips or pellets, are usually formed into the container shape in a two stage process. First, a container preform is injection molded; and second, either immediately or after a short storage period, the container preform is blown using compressed air into a mold which is in the final shape of the container. In the second stage of the process, the container preform is usually at or near ambient temperature, and it has to be heated to a temperature (for PET) of from about 85°C to about 120°C for the blow molding step. It is this

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"reheat" step which is usually the rate-determining step in the second stage of the process.

Accordingly, to increase the output of the container-forming processes, known energy-absorbing materials have been added to polymer compositions to increase the "reheat" rate of the polymer preform to be processed and made into a container. By increasing the reheat rate, less energy and time is required to heat the polymer preform to its glass transition temperature ( $T_g$ ) and blow mold the preform thereby forming a container. Thus, the output of the container-forming processes is increased and less energy is required when using reheat rate-increasing additives. Examples of such known energy-absorbing materials or reheat rate-increasing additives and compositions containing same are illustrated in U.S. Patents 4,408,004; 4,476,272; 4,535,118; 4,420,581; 5,419,936; and 5,529,744.

However, none of the processes utilizing reheat rate-increasing additives in thermoplastic polymers incorporate a reheat additive in a process where crystallization of a polymer containing the additive is carried out. Previously, it was thought that there was no correlation or connection between reheat rate-increasing additives and polymer crystallization. In fact, prior to the present invention, there was no indication or expectation that such additives would have a significant affect on polymer crystallization, crystallization rates, or crystallization processes.

## 2. *Crystallization in Blow Molding Applications*

Thermoplastic polymers are often heat-treated to modify their material characteristics for improved performance when forming thermoplastic articles. For example, the finishes (i.e., the upper portion typically comprising an opening and threads for engaging a cap) of PET preforms made to be blow molded into heat-set containers are commonly crystallized by heating the finish of the preform, typically by exposure to infrared (IR) radiation. The purpose of subjecting heat-set preforms to this process, known as the Yoshino Process (U.S. Patent 5,261,545), is to convert the amorphous material in this region of the container to crystalline form, and

thereby prevent or reduce distortion of the finish of the heat-set container during hot filling.

In the Yoshino Process, an injection-molded preform is placed in a carrier which shields the body of the preform against exposure to crystallizing heat, but  
5 leaves the finishes exposed. The carrier containing the preform passes through an oven, where the preform finish is exposed to infrared energy for a sufficient amount of time to allow the finish to highly crystallize. High crystallinity provides dimensional stability to the finish and allows the resulting article or container to be hot-filled without suffering from thermal distortion in the finish.

10 However, not all polymers can be used for forming containers according to the Yoshino process. Copolymers, for example, have much slower crystallization rates than homopolymers. Therefore, using copolymers in the Yoshino process provides less throughput and requires more energy than homopolymers. Prior to the present invention, homopolymers were the predominant polymer used in  
15 crystallization processes.

Moreover, unfortunately, crystallizing a thermoplastic polymer preform is an additional step in the conventional container-forming process. An additional step, of course, creates longer and less efficient processing. Several factors effect the rate at which the crystallizing machine can process preforms, including polyester resin  
20 properties, oven efficiency, temperature the preform attains in the oven, and time spent in the oven. Accordingly, increasing efficiency by minimizing the amount of time and additional energy required to complete the container-forming process having a crystallization step is still needed.

Thus, heretofore, efficiency of a manufacturing facility crystallizing (at least  
25 a portion thereof) preforms processed under a Yoshino-type process was not enhanced by increasing the crystallization rate of preforms through the use of a reheat rate-increasing additive. In addition, only homopolymers were useful in applications requiring faster crystallization because copolymers were limited by their slower crystallization rates. Moreover, there was no indication or expectation that a

reheat rate-increasing additive would have any affect on, let alone increase polymer (homopolymer and copolymer) crystallization, crystallization rates, or crystallization processes.

### Summary of the Invention

5       The method of the present invention uses a polymer/reheat rate-increasing additive composition to increase the rate of the polymer crystallization and, thus, the efficiency of a conventional container-forming process.

In accordance with the purpose(s) of this invention, as embodied and broadly described herein, this invention, in one aspect, relates to a method of producing a  
10 thermoplastic polymer preform having at least a crystalline finish portion comprising (i) providing a thermoplastic polymer composition comprising a thermoplastic polymer and at least one reheat rate-increasing additive; (ii) forming a preform from the thermoplastic polymer composition, wherein the preform comprises a finish portion and a body portion; and (iii) exposing at least the finish portion of the  
15 preform to energy until crystallized.

In another aspect, the present invention relates to a method of producing a thermoplastic polymer container having at least a crystalline finish portion, the method comprising (i) providing a thermoplastic polymer composition comprising a thermoplastic polymer and at least one reheat rate-increasing additive; (ii) forming a  
20 preform from the thermoplastic polymer composition, wherein the preform comprises a finish portion and a body portion; (iii) exposing at least the finish portion of the preform to energy until crystallized; and (iv) blow molding the preform into a container, wherein the container has at least a crystalline finish portion.

25       In another aspect, the present invention relates to a method of crystallizing at least a finish portion of a thermoplastic polymer container comprising (i) providing a thermoplastic polymer container comprising a thermoplastic polymer and at least one reheat rate-increasing additive, wherein the container has a finish portion and a

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body portion; and (ii) exposing at least the finish portion of the container to energy until crystallized.

In yet another aspect, the present invention relates to a method of crystallizing a thermoplastic polymer composition comprising (i) providing a thermoplastic polymer composition comprising a thermoplastic polymer and at least one reheat rate-increasing additive; and (ii) exposing at least a portion of the composition to energy until crystallized.

In still another aspect, the present invention relates to a method for forming containers comprising a heat-set finish on a portion of the container comprising (i) molding a container from a polymer comprising at least one reheat rate-improving additive; and (ii) heat-setting at least a portion of the finish of the container.

In yet another aspect, the present invention relates to a container formed from a thermoplastic polymer comprising a body and a finish, wherein the finish is crystalline and contains a reheat rate-increasing additive.

In other aspects, the present invention relates to products made by the processes of the present invention.

Additional advantages of the invention will be set forth in part in the detailed description, including the figures, which follows, and in part will be obvious from the description, or may be learned by practice of the invention. The advantages of the invention will be realized and attained by means of the elements and combinations particularly pointed out in the appended claims. It is to be understood that both the foregoing general description and the following detailed description are exemplary and explanatory of preferred embodiments of the invention, and are not restrictive of the invention, as claimed.

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#### **Brief Description of the Figures**

Figure 1 is a plot of crystallinity (weight percent) of six PET polymers versus radiant energy exposure (watts) of the polymers over a 32.2 second period. The

polymers having the reheat rate-increasing additive therein have the highest crystallinity.

Figure 2 is a plot of crystallinity (weight percent) of six PET polymers versus production rate (parts/minute) of the polymers. Two of the polymers having the reheat rate-increasing additive therein show higher crystallinity at the same lower production rate indicating a faster crystallization rate for those polymers having the additive.

### **Detailed Description of the Invention**

The present invention may be understood more readily by reference to the following detailed description of the invention, including the appended figures referred to herein, and the examples provided therein. It is to be understood that this invention is not limited to the specific processes and conditions described, as specific processes and/or process conditions for processing plastic articles as such may, of course, vary. It is also to be understood that the terminology used herein is for the purpose of describing particular embodiments only and is not intended to be limiting.

It must also be noted that, as used in the specification and the appended claims, the singular forms "a," "an" and "the" include plural referents unless the context clearly dictates otherwise. For example, reference to processing a thermoplastic "preform," "article," "container" or "bottle" is intended to include the processing of a plurality of thermoplastic preforms, articles, containers or bottles.

Ranges may be expressed herein as from "about" or "approximately" one particular value and/or to "about" or "approximately" another particular value. When such a range is expressed, another embodiment includes from the one particular value and/or to the other particular value. Similarly, when values are expressed as approximations, by use of the antecedent "about," it will be understood that the particular value forms another embodiment.

It has been discovered that the rate and percent of crystallization of an amorphous thermoplastic polymer can be increased by incorporating into the



polymer a reheat rate-increasing additive before processing by a crystallization machine. "Amorphous," for purposes of further defining the polymers of the present invention prior to crystallization, shall mean substantially noncrystalline. A substantially noncrystalline polymer typically may have less than about 5 to 7  
5 weight percent crystallinity. In particular, and by way of example, significant increases in the efficiency of processing heat-set PET container preforms having a crystallized finish portion using the Yoshino process may be obtained by means of the method described herein.

In a broad sense, the process aspects of the invention may be defined as a  
10 method of producing molded articles comprising preparing a preform of thermoplastic polymer admixed with a reheat rate-increasing additive, subjecting the preform to radiant energy for a period of time necessary to raise its temperature to above the glass transition temperature of the polymer, and subsequently forming the preform into a desired shape. The term "glass transition temperature" is defined  
15 generally as the temperature at which the polymer changes from a glass-like material to a rubbery or leathery material.

The present invention is highly useful because 1) the method increases the amount of reheat energy which is absorbed by the preforms, and 2) the method increases (nucleates) the spherulitic crystalline growth rate during the step of  
20 preform/container crystallization. Spherulitic crystalline growth may be defined as the increase in spheroid crystalline bodies in the amorphous polymer.

Moreover, it has been surprisingly found that conventional reheat additives improve crystallization from the glass (providing improved processing during the finishing step), but do not noticeably affect the crystallization from the melt. This is  
25 particularly important because significant changes in crystallization from the melt would result in narrowed processing windows, which would make container production more difficult and less forgiving.

Thus, the method of the present invention provides preforms/containers having a higher or increased degree of crystallinity in a shorter processing time. The

method of the present invention further provides a container-forming and/or container-processing step having increased output rates.

Presently Preferred Embodiments

Briefly described, in one presently preferred embodiment, the present invention comprises a method of producing a thermoplastic polymer preform having at least a crystalline finish portion. The method comprises (i) providing a thermoplastic polymer composition comprising a thermoplastic polymer and at least one reheat rate-increasing additive; (ii) forming a preform from the thermoplastic polymer composition, wherein the preform comprises a finish portion and a body portion; and (iii) exposing at least the finish portion of the preform to energy until crystallized. The invention also relates to a preform produced by the method of this embodiment.

In a second embodiment, the present invention relates to a method of producing a thermoplastic polymer container having at least a crystalline finish portion. This method comprises (i) providing a thermoplastic polymer composition comprising a thermoplastic polymer and at least one reheat rate-increasing additive; (ii) forming a preform from the thermoplastic polymer composition, wherein the preform comprises a finish portion and a body portion; (iii) exposing at least the finish portion of the preform to energy until crystallized; and (iv) blow molding the preform into a container, wherein the container has at least a crystalline finish portion. Preferably, the preform in step (iv) is at a temperature of from 80°C to 125°C for blow molding. The invention also relates to a container produced by the method of this second embodiment.

In a third embodiment, the present invention relates to a method of crystallizing at least a finish portion of a thermoplastic polymer container comprising (i) providing a thermoplastic polymer container comprising a thermoplastic polymer and at least one reheat rate-increasing additive, wherein the container has a finish portion and a body portion; and (ii) exposing at least the finish portion of the container to energy until crystallized. This embodiment differs from

that of exposing a preform to energy until crystallized. In this embodiment, at least the finish portion of a container, not a preform, is exposed to crystallizing energy. The invention also relates to a container crystallized by the method of this third embodiment.

5 In yet another embodiment, the present invention relates to a method of crystallizing a thermoplastic polymer composition. The method comprises (i) providing a thermoplastic polymer composition comprising a thermoplastic polymer and at least one reheat rate-increasing additive; and (ii) exposing at least a portion of the composition to energy until crystallized. This embodiment is different in that at  
10 least a portion of a composition having an additive is exposed to crystallizing energy and not a finish of a preform or a container. Preferably, the thermoplastic polymer composition is in the form of an article, more preferably a container, and even more preferably a bottle. Moreover, the invention relates to a bottle crystallized by the method of this embodiment.

15 In yet another embodiment, this invention relates to a method for forming containers comprising a heat-set finish on a portion of the container comprising (i) molding a container from a polymer comprising at least one reheat rate-improving additive; and (ii) heat-setting at least a portion of the finish of the container. Preferably, the reheat rate-improving additive is carbon black, iron oxide or  
20 antimony metal. More preferably, the polymer comprises antimony metal in a concentration of about 20 ppm (ppm = parts per million by weight) or more, iron oxide in a concentration of less than about 12 ppm or carbon black in a concentration of less than about 10 ppm. The invention also relates to a container formed from the method of this embodiment.

25 In another embodiment, the present invention relates to a container formed from a thermoplastic polymer. The container comprises a body and a finish, wherein the finish is crystalline and contains a reheat rate-increasing additive. Preferably, the finish is at least 25 weight percent crystalline. Preferably, the thermoplastic polymer used for forming the container is poly(ethylene terephthalate) or a copolymer  
30 thereof. The reheat rate-increasing additive preferably includes, but is not limited to,

carbon black, iron oxide, antimony, tin, copper, silver, gold, palladium, platinum or a mixture thereof.

In all of the embodiments of this invention, the thermoplastic polymer composition is preferably transparent. Further, the thermoplastic polymer may  
5 comprise a homopolymer or comprise a copolymer. Preferably, the polymer is a polyester, and more preferably poly(ethylene terephthalate) or a copolymer thereof.

Exposure to energy to crystallize at least the finish portion of the preform or container having the additive is effected for about 25 seconds. The finish of the preform is at least 20 weight percent crystalline after exposure to crystallizing  
10 energy. Preferably, the crystallizing radiant energy is at least partially within the infrared region of the energy spectrum. Further, at least a portion of the preform crystallizes at a rate faster than that of a preform without a reheat rate-increasing additive.

#### Thermoplastic Polymers

15 The thermoplastic polymer used in the invention is most usually a polyester, particularly a partially aromatic polyester, especially a polyester derived, at least mainly, from an aromatic diacid and an aliphatic (including cycloaliphatic) diol. A preferred partially aromatic polyester is one which comprises at least 50 mole %, preferably at least 70 mole %, of ethylene terephthalate residues. The polyester may  
20 also contain residues derived from ethylene isophthalate, ethylene naphthalate, ethoxyethylene terephthalate, ethoxyethylene isophthalate or ethoxyethylene naphthalate.

Typically, polyesters such as polyethylene terephthalate polymer (PET) are made by reacting a glycol with a dicarboxylic acid as the free acid or its dimethyl  
25 ester to produce a prepolymer compound which is then polycondensed to produce the polyester. If required, the molecular weight of the polyester can then be increased further by solid state polymerization.

Suitable polyesters for the method of the present invention include crystallizable polyester homopolymers or copolymers that are suitable for use in

containers and packaging, and particularly food packaging. The present invention provides accelerated crystallization rates for any thermoplastic resins, e.g., PET containing a reheat rate-increasing additive. Suitable polyesters are generally known in the art and may be formed from aromatic dicarboxylic acids, esters of  
5 dicarboxylic acids, anhydrides of dicarboxylic esters, glycols, and mixtures thereof. More preferably, the polyesters are formed from repeat units comprising terephthalic acid, dimethyl terephthalate, isophthalic acid, dimethyl isophthalate, dimethyl-2,6-naphthalenedicarboxylate, 2,6-naphthalenedicarboxylic acid, ethylene glycol, diethylene glycol, 1,4-cyclohexane-dimethanol, 1,4-butanediol, and mixtures  
10 thereof.

The dicarboxylic acid component of the polyester may optionally be modified with one or more different dicarboxylic acids. Such additional dicarboxylic acids include aromatic dicarboxylic acids preferably having 8 to 14 carbon atoms, aliphatic dicarboxylic acids preferably having 4 to 12 carbon atoms,  
15 or cycloaliphatic dicarboxylic acids preferably having 8 to 12 carbon atoms. Examples of dicarboxylic acids to be included with terephthalic acid are: phthalic acid, isophthalic acid, naphthalene-2,6-dicarboxylic acid, cyclohexanedicarboxylic acid, cyclohexanediacetic acid, diphenyl-4,4'-dicarboxylic acid, succinic acid, glutaric acid, adipic acid, azelaic acid, sebacic acid, mixtures thereof and the like.  
20 Preferably, the amount of said second dicarboxylic acid is less than 30 mole% and more preferably less than about 15 mole%.

In addition, the glycol component may optionally be modified with one or more different glycols other than ethylene glycol. Such additional glycols include cycloaliphatic diols preferably having 6 to 20 carbon atoms or aliphatic diols  
25 preferably having 3 to 20 carbon atoms. Examples of such glycols include: diethylene glycol, triethylene glycol, 1,4-cyclohexanedimethanol, propane-1,3-diol, butane-1,4-diol, pentane-1,5-diol, hexane-1,6-diol, 3-methylpentanediol-(2,4), 2-methylpentanediol-(1,4), 2,2,4-trimethylpentane-diol-(1,3), 2-ethylhexanediol-(1,3), 2,2-diethylpropane-diol-(1,3), hexanediol-(1,3), 1,4-di-(hydroxyethoxy)-benzene,  
30 2,2-bis-(4-hydroxycyclohexyl)-propane, 2,4-dihydroxy-1,1,3,3-tetramethyl-

cyclobutane, 2,2-bis-(3-hydroxyethoxyphenyl)-propane, 2,2-bis-(4-hydroxypropoxyphenyl)-propane, mixtures thereof and the like. Polyesters may be prepared from two or more of the above glycols. Preferably, the amount of the second glycol is less than 30 mole% and more preferably less than about 15 mole%.

- 5       The thermoplastic resin may also contain small amounts of trifunctional or tetrafunctional comonomers such as trimellitic anhydride, trimethylolpropane, pyromellitic dianhydride, pentaerythritol, and other polyester forming polyacids or polyols generally known in the art.

Reheat Rate-Increasing Additives

- 10       As described above, the thermoplastic polymers according to this invention include at least one reheat rate-increasing additive. Reheat rate is defined as the change in average temperature of a molded part as a function of exposure to a radiant heat source for a specified time. Suitable reheat rate-increasing additives are well known in the art and include, preferably, black and gray body absorbers such as
- 15       carbon black, antimony metal, iron oxide and the like, as well as near infrared absorbing dyes, including, but not limited to those disclosed in U.S. 97/15351, which is incorporated herein by reference.

- 20       The reheat rate-increasing additive should be present in an amount sufficient to improve the reheat rate of an unmodified polymer. The actual amount of reheat rate-increasing additive will vary depending on which additive is used. Typically, in order to achieve the presently preferred crystallization of a preform or container, the thermoplastic polymer composition comprises the reheat rate-increasing additive in a concentration of about 1 to 300 ppm. The reheat rate-increasing additive may be
- 25       typically any reheat rate-increasing additive used in the art, including, but not limited to, carbon black, iron oxide, antimony, tin, copper, silver, gold, palladium, platinum or a mixture thereof. However, only very small amounts of black body absorbers, like carbon black and iron oxide (about 10-12 ppm or less) may be necessary to achieve the desired crystallinity, but relatively large amounts of gray
- 30       body absorbers like antimony metal may be necessary to achieve the same effect.

Typically, the polymer composition may comprise antimony metal in a concentration of at least 10 ppm.

The more effective concentration of the iron oxide, for example, is from about 1.0 to about 100 ppm, preferably from about 1 to about 50 ppm with 1-30 ppm being most preferred. The iron oxide, preferably  $\text{Fe}_2\text{O}_3$ , is used in very finely divided form e.g., from about 0.01 to about 200  $\mu\text{m}$ , preferably from about 0.1 to about 10.0  $\mu\text{m}$ , and most preferably from about 0.2 to about 5.0  $\mu\text{m}$ . Such oxides are described, for example, on pages 323-349 of Pigment Handbook, Vol. 1, copyright 1973, John Wiley & Sons, Inc.

Iron oxide, for example, can be added to the polyester reactant system, during or after polymerization, to the polyester melt, or to the molding powder or pellets from which the bottle preforms are formed. For purposes of clarification, the bottle preforms are test tube shaped, injection moldings which are heated above the glass transition temperature of the polymer and then positioned in the bottle mold to receive the pressurized air through its open end. Such technology is well known to the art as shown in U.S. Pat. No. 3,733,309. Any radiant energy source may be employed, and the one used for heating the preforms according to this invention is a quartz lamp, Model Q-1P, 650 W., 120 V., by Smith Victor Corp.

Suitable preferred metals for use as the additive according to the method of this invention include antimony, tin, copper, silver, gold, palladium and platinum or a mixture of two or more of these. It should also be appreciated that additional gray and black body absorbers including, but not limited to arsenic, cadmium, mercury and lead can also be used. However, for most applications, silver, gold, arsenic, cadmium, mercury, lead, palladium and platinum are either too expensive or environmentally hazardous and these metals are, consequently, not particularly preferred. Preferably, the metal is one or more of antimony, tin or copper with antimony being particularly advantageous.

Moreover, if metal is used as the reheat rate-increasing additive, the metal preferably is in particle form for ease of processing. The metal particles are

preferably sufficiently fine for them not to be visible to the eye and have a range of sizes such that absorption of radiation occurs over a relatively wide part of the wavelength range and not just at one particular wavelength or over a narrow band.

The amount of metal particles present in the thermoplastic polymer composition, as it is to be used in this invention, is a balance between the desired reduction in the reheat time of the polymer, the crystallization of the polymer and the amount of haze that is acceptable for a given application. Preferably, the amount of metal particles is from about 1 ppm to 300 ppm, more particularly from about 5 ppm to 150 ppm, and especially from about 10 ppm to 100 ppm. If desired, masterbatches of the polymer composition containing quantities of metal particles in far higher concentrations can be made for subsequent blending with polymer essentially free from the metal particles to achieve the desired levels of particles.

In polyester compositions, antimony is especially preferred because, in the form of antimony trioxide (antimony (III) oxide), it is a catalyst for the polymerization of the monomers used in the preparation of polyesters such as poly(ethylene terephthalate). As the polyester monomer melt is a slightly reducing environment, the polyesters may naturally have a very minor proportion of antimony metal present, e.g., up to about 5-6 ppm. However, these low levels of antimony metal do not affect the reheat time significantly.

Also, although not required, additives and/or lubricants normally used in polyesters may be used if desired. Such additives include catalysts, colorants, pigments, glass fibers, fillers, impact modifiers, antioxidants, stabilizers, processing aids, flame retardants, acetaldehyde reducing compounds and the like.

#### Typical Technique for Producing a Thermoplastic Container

The method of the present invention is particularly suited for use in the production of a heat-set thermoplastic polymer (e.g., polyester) container. A polyester preform, for example, is molded in the injection molding machine from a polyester resin containing a reheat rate-increasing additive. The preform is molded according to known techniques, whereby polyester pellets are dried and injection.



molded to produce clear, amorphous polyester preforms. The amorphous or "glassy" preforms preferably comprise a threaded finish portion and a body portion. The finish portion is crystallized according to the present invention to prevent distortion of the finish upon further processing of the preform to produce a container, or upon  
5 heat-filling of the container. The body portion of the preform is typically processed, as by heated blow molding, to form a container having a desired shape and size.

According to the present invention, a portion of the preform is crystallized. Preferably, only the finish is crystallized. Crystallization of the finish is usually an optional, and, until now, predominantly cumbersome stage of a preform-forming  
10 process. However, by using a reheat rate-increasing additive in accordance with this invention, crystallization rates are dramatically increased rendering a crystallization stage more desirable in many container-forming applications.

Generally, crystallization involves exposing at least a portion of the preform finish to radiant heat from lamps in a row of ovens (across a spectrum which may  
15 include the IR range) while protecting the body of the preform.

More particularly, after forming the preform, the preform is transported to a crystallization machine. The preforms are preferably loaded into carriers which shield the bodies of the preforms against exposure to crystallizing heat, but leave the finishes exposed. The carriers, containing the preforms, are passed through the  
20 crystallizing machine, where the preform finishes are exposed to infrared energy for a sufficient amount of time to allow the finishes to crystallize. This stage preferably involves exposing at least a portion of the preform finish to radiant heat from lamps in a row of ovens (across a spectrum that may include the IR range) while protecting the body of the preform. The finish is heated to temperatures at which the selected  
25 polyester crystallizes rapidly (for PET about 150°C to about 180°C). This results in a highly crystalline finish, i.e., spherulitic crystallinity levels at a minimum of about 20 weight percent. These high levels of crystallinity give dimensional stability to the finish that enable the resulting container to be hot-filled without suffering from thermal distortion in the finish region. Moreover, at least a portion of the preform

crystallizes at a rate faster than that of a preform without a reheat rate-increasing additive.

Crystallization of the finish can be performed either to the preform (as in the Yoshino process), to a pre-bottle (as in the Sidel SRCF process outlined in U.S. Patent No. 5,382,157), or to the actual heat-set bottle.

The desired container is preferably blow molded from the preform and heat-set, according to known techniques. In particular, the preform body (with or without the crystallized finish) is exposed lamps emitting radiant heat (which may include the IR range of the spectrum) until the preform has reached the appropriate temperature range for bottle blowing (from about 85°C to about 120°C for PET). The preform is removed from the oven and placed into a warm or hot blow mold and pressurized. The preform is thereby stretched into a container, preferably a bottle which is held against the warm or hot blow mold (therefore, the name "heat-set"). These bottles are typically designed to withstand hot-filling without shrinkage greater than about 1% by volume. It is also desirable, although not required, to achieve a large degree of spherulitic crystallinity in the bottle sidewall in order to resist thermal distortion upon hot-filling of the bottle.

Crystallization of the bottle preforms occurs through crystal nucleation. Crystal nucleation in the preform is primarily heterogeneous. That is, the initial seed crystal forms at the surface of a pre-existing foreign particle in the resin, in the present case, a reheat rate-increasing additive. The additive, in accordance with the present invention, is a component intentionally added to promote increased reheat rates and nucleation. The density of crystal nucleation is controlled by the density of the additive as well as the rate at which seed crystals of polymer form at the surface of the additive, which is in turn influenced by material variables and temperature.

### Examples

The following examples and experimental results are included to provide those of ordinary skill in the art with a complete disclosure and description of particular manners in which the present invention can be practiced and evaluated,

and are intended to be purely exemplary of the invention and are not intended to limit the scope of what the inventors regard as their invention. Efforts have been made to ensure accuracy with respect to numbers (e.g., amounts, temperature, etc.); however, some errors and deviations may have occurred. Unless indicated  
5 otherwise, parts are parts by weight, temperature is in °C or is at ambient temperature, and pressure is at or near atmospheric.

Thus, it has been discovered that incorporating a reheat rate-increasing additive into PET, for example, dramatically accelerates the crystallization rate of PET from the glass. However, the decisive factor in determining whether this effect  
10 is useful in commercial package manufacturing processes is how long the PET article must be exposed to crystallizing energy. In general, the longer the required exposure time to achieve accelerated crystallization, the less the process is commercially attractive.

The following example(s), in addition to the figures discussed above,  
15 illustrate that the required exposure time to achieve accelerated crystallization is much less for those compositions containing a reheat rate-increasing additive than those compositions without the additive.

#### **Production of Heat-Set Thermoplastic Polymer (PET) Preforms**

##### **1) Injection Molding**

20 A polymer preform was injection molded. Specifically, preblended polymer (PET Homopolymer or modified PET) pellet concentration @ 50:1 let down ratio resulting in a 12 ppm level of black iron oxide was formed. Preforms were molded from the blend on a standard injection molding machine (4-cavity Husky LX-160). This injection molding machine is well known to one of ordinary skill in the art and,  
25 as such, need not be described in detail here.

##### **2) Reheat - Crystallizing**

The preforms were crystallized on standard reheat equipment (Sidel SBO 2/3), which typically can be a stretch blow molding machine. This equipment is

well known to one of ordinary skill in the art and, as such, need not be described in detail here. To simulate finish crystallization process, preforms were subjected to the following various heating times and/or energy exposure levels to a point at which crystallization of the preform body occurred:

- 5           (1)    the radiant energy exposure was changed while holding production output rate constant (32.2 second period) (energy range: 250,000 to 475,000 watts) (Figure 1); and
- (2)    the exposure time was changed by varying production output rate while holding lamp intensity constant (output range: 8-13.5
- 10           parts/minute) (Figure 2).

3)    Testing

The crystallinity of the preforms was determined by first measuring gradient tube density, then converting density to weight percent crystallinity using the equations standard to the industry. Both measuring gradient tube density and

15    converting density to crystallinity using standard equations are known to one of ordinary skill in the art and, as such, need not be described in detail here. The results of the examples tested are illustrated in Figures 1 and 2.

**Comparative Example**

A PET Homopolymer preform with approximately 12 ppm black iron oxide

20    was prepared by the method outlined above and subjected to approximately 475,000 watts of exposure of IR over a 32.2 second period. The preform developed 41 weight percent crystallinity.

The same PET Homopolymer preform was prepared without the black iron oxide and subjected to the same exposure conditions. This preform developed only

25    10 weight percent crystallinity.

Referring now to the figures, Figure 1 is a plot of experimental results demonstrating the crystallinity (weight percent) of various forms of PET after exposure to radiant energy (watts) over the 32.2 second reheat period. Figure 2 is a

plot of experimental results demonstrating the crystallinity (weight percent) of the PET forms versus the production rate of the preforms. The results graphed in Figures 1 and 2 refer to the following forms of PET manufactured and used by Eastman Chemical Corporation of Kingsport, Tennessee, U.S.A.:

- 5           a) 0.8 ItV (intrinsic viscosity) PET homopolymer (EASTAPAK 9663) with and without a reheat rate-increasing additive;
- b) 0.8 ItV CHDM (cyclohexane dimethanol) modified PET (EASTAPAK (R) copolyester 9921W) with and without a reheat rate-increasing additive, and
- 10          c) 0.8 ItV IPA (isophthalic acid) modified PET (at Eastman Chemical Company referred to internally as EASTAPAK (R) copolyester B-11) with and without a reheat rate-increasing additive.

With reference to Figure 1 in particular, three forms of PET (all with 0.8 ItV) contain a reheat rate-increasing additive in accordance with the method of this invention: PET Homopolymer; CHDM Modified PET; and IPA Modified PET.

15           Figure 1 illustrates that at the end of the reheat period (32.2 seconds), wherein the PET forms are exposed to a final radiant energy of approximately 450,000 watts, the three above-mentioned PET forms having the reheat additive clearly have a higher crystallinity than those without the reheat additive.

20           In addition, it is particularly surprising that the PET copolymers (CHDM and IPA modified) have a higher crystallinity than the PET homopolymer without a reheat additive. Copolymers, in general, do not crystallize as fast as homopolymers. Therefore, Figure 1 clearly indicates that the addition of a reheat rate-increasing additive dramatically increases the crystallinity of a homopolymer and a copolymer.

25           Experimental evidence in Figure 1 confirms this proposition because the PET homopolymer having the additive has a higher crystallinity at the end of the reheat period than the PET copolymers with an additive. This result is to be expected given the crystallization rates of homopolymers versus copolymers.

Referring particularly to Figure 2, a plot of crystallization of the PET polymers versus the production rate indicates again that the crystallization of the PET polymers having the reheat rate-increasing additive is markedly increased over those PET polymers without the additive. For example, at lower production rates (8-10 parts/minute), the 0.8 PET Homopolymer and 0.8 ItV CHDM modified PET having the reheat additive show over double (at 8 parts/minute) the crystallinity of those PET polymers without the additive. These results strongly suggest that 1) the rate of crystallization of the PET polymers with the additive is significantly higher than those without the additive, and 2) the reheat rate-increasing additive is the reason for the dramatic increase in the rate of crystallization. First, the PET polymers are the same (*i.e.*, 0.8 ItV and modified with the same copolymers). Second, the processing conditions are the same (*i.e.*, temperature, time, rate, exposure to energy). Therefore, the only experimental variable that distinguishes the results shown in Figure 2 is the reheat rate-increasing additive, and the results show that the additive dramatically improves crystallization of the PET polymers.

Throughout this application, various publications are referenced. The disclosures of these publications in their entireties are hereby incorporated by reference into this application in order to more fully describe the state of the art to which this invention pertains.

It will be apparent to those skilled in the art that various modifications and variations can be made in the present invention without departing from the scope or spirit of the invention. Other embodiments of the invention will be apparent to those skilled in the art from consideration of the specification and practice of the invention disclosed herein. It is intended that the specification and examples be considered as exemplary only, with a true scope and spirit of the invention being indicated by the following claims.

**What is Claimed is:**

1. A method of producing a thermoplastic polymer preform having at least a crystalline finish portion comprising:
  - (i) providing a thermoplastic polymer composition comprising a thermoplastic polymer and at least one reheat rate-increasing additive;
  - (ii) forming a preform from the thermoplastic polymer composition, wherein the preform comprises a finish portion and a body portion; and
  - (iii) exposing at least the finish portion of the preform to energy until crystallized.
2. The method of Claim 1, wherein the thermoplastic polymer composition is amorphous.
3. The method of Claim 1, wherein the thermoplastic polymer comprises a homopolymer.
4. The method of Claim 1, wherein the thermoplastic polymer comprises a copolymer.
5. The method of Claim 1, wherein the thermoplastic polymer comprises a polyester.
6. The method of Claim 5, wherein the polyester is poly(ethylene terephthalate) or a copolymer thereof.
7. The method of Claim 1, wherein the thermoplastic polymer composition comprises the reheat rate-increasing additive in a concentration of from about 1 to 300 ppm.
8. The method of Claim 1, wherein the reheat rate-increasing additive is carbon black, dyes, iron oxide, antimony, tin, copper, silver, gold, arsenic, cadmium, mercury, lead, palladium, platinum or a mixture thereof.

9. The method of Claim 1, wherein the reheat rate-increasing additive comprises iron oxide in a concentration of from about 1 to 60 ppm.
10. The method of Claim 9, wherein the iron oxide is  $\text{Fe}_2\text{O}_3$  and has a particle size from about 0.1 to 10  $\mu\text{m}$ .
11. The method of Claim 1, wherein the reheat rate-increasing additive comprises antimony metal in a concentration of at least 3 ppm.
12. The method of Claim 1, wherein step (iii) is effected for at least 25 seconds.
13. The method of Claim 1, wherein the finish portion of the preform is at least 25 weight percent crystalline after step (iii).
14. The method of Claim 1, wherein only the finish portion is exposed to energy to crystallize it in step (iii).
15. The method of Claim 1, wherein the energy is radiant energy.
16. The method of Claim 15, wherein the radiant energy is at least partially within the infrared region of the energy spectrum.
17. A preform produced by the method of Claim 1.
18. A method of crystallizing at least a finish portion of a thermoplastic polymer container comprising:
  - (i) providing a thermoplastic polymer container comprising a thermoplastic polymer and at least one reheat rate-increasing additive, wherein the container has a finish portion and a body portion; and
  - (ii) exposing at least the finish portion of the container to energy until crystallized.
19. The method of Claim 18, wherein the thermoplastic polymer is amorphous.
20. The method of Claim 18, wherein the thermoplastic polymer comprises a polyester homopolymer or copolymer.



21. The method of Claim 20, wherein the polyester is poly(ethylene terephthalate) or a copolymer thereof.
22. A container crystallized by the method of Claim 18.
23. A method of producing a thermoplastic polymer container having at least a crystalline finish portion comprising:
  - (i) providing a thermoplastic polymer composition comprising a thermoplastic polymer and at least one reheat rate-increasing additive;
  - (ii) forming a preform from the thermoplastic polymer composition, wherein the preform comprises a finish portion and a body portion;
  - (iii) exposing at least the finish portion of the preform to energy until crystallized; and
  - (iv) blow molding the preform into a container, wherein the container has at least a crystalline finish portion.
24. The method of Claim 23, wherein the thermoplastic polymer composition is amorphous.
25. The method of Claim 23, wherein the preform in step (iv) is at a temperature of from 80°C to 125°C.
26. A container produced by the method of Claim 23.
27. A method of crystallizing a thermoplastic polymer composition comprising:
  - (i) providing a thermoplastic polymer composition comprising a thermoplastic polymer and at least one reheat rate-increasing additive; and
  - (ii) exposing at least a portion of the composition to energy until crystallized.

28. The method of Claim 27, wherein the thermoplastic polymer composition is amorphous.
29. The method of Claim 27, wherein the thermoplastic polymer composition is in the form of an article.
30. The method of Claim 29, wherein the article is a container.
31. The method of Claim 30, wherein the container is a bottle.
32. A bottle crystallized by the method of Claim 31.
33. A method for forming a container comprising a heat set finish on a portion of the container comprising:
  - (i) molding a container from a polymer comprising at least one reheat rate-improving additive; and
  - (ii) heat setting at least a portion of the finish of the container.
34. The method of Claim 33, wherein the reheat rate-improving additive is carbon black, iron oxide or antimony metal.
35. The method of Claim 33, wherein the polymer comprises antimony metal in a concentration of about 20 ppm or more.
36. The method of Claim 33, wherein the polymer comprises iron oxide in a concentration of greater than 0 to less than about 12 ppm.
37. The method of Claim 33, wherein the polymer comprises carbon black in a concentration of greater than 0 to less than about 12 ppm.
38. A container formed by the method of Claim 33.
39. A container formed from a thermoplastic polymer comprising:
  - a body; and
  - a finish, wherein the finish is crystalline and contains a reheat rate-increasing additive.

40. The container of Claim 39, wherein the thermoplastic polymer is poly(ethylene terephthalate) or a copolymer thereof.
41. The method of Claim 39, wherein the reheat rate-increasing additive is carbon black, iron oxide, antimony, tin, copper, silver, gold, arsenic, cadmium, mercury, lead, palladium, platinum or a mixture thereof.
42. The method of Claim 39, wherein the finish is at least 20 weight percent crystalline.

# INTERNATIONAL SEARCH REPORT

International Application No  
PCT/US 99/11659

A. CLASSIFICATION OF SUBJECT MATTER  
IPC 6 C08J3/20 B29C71/02 C08K3/00

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C08J B29C C08K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 94 10242 A (ALLIED SIGNAL INC) 11 May 1994 (1994-05-11) page 9, line 2 - page 10, line 3 page 3, line 33 - page 4, line 30 claims 6-10	1-8
A	US 5 419 936 A (TINDALE NEIL) 30 May 1995 (1995-05-30) cited in the application claims 1-6	1-42
A	US 4 535 118 A (PENGILLY BRIAN W) 13 August 1985 (1985-08-13) cited in the application examples column 6-9 claim 1	1-42

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

### \* Special categories of cited documents :

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

- "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- "&" document member of the same patent family

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# INTERNATIONAL SEARCH REPORT

information on patent family members

International Application No

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